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Microwave Assisted Synthesis and Characterization of Glycidyl Azide Polymers Containing Different Initiating Diol Units

Ajay KSHIRSAGAR, Vikas GITE, Dilip HUNDIWALE, Pramod MAHULIKAR*

School of Chemical Sciences, North Maharashtra University, P.B. No.80, Jalgaon − 425 001, (M.S.) India
**E-mail: mahulikarpp@rediffmail.com*

Abstract: Glycidyl azide polymers (GAPs), containing different initiating diol units were prepared by treating the corresponding poly(epichlorohydrins) (PECHs) with sodium azide under microwave irradiation (600 W power) at 80 °C, during 12 min. The PECHs containing different diol units were synthesized by the polymerization of epichlorohydrin using borontrifluoride etherate as initiator in the presence of small amounts of low molecular weight diols. The synthesized PECHs and GAPs, containing different initiating diol units, were characterized by various spectroscopic techniques and by thermal analysis (DSC). These results are reported and discussed.

Keywords: glycidyl azide polymer, poly(epichlorohydrin), cationic ring-opening polymerization, microwave irradiation, thermal properties

1 Introduction

In recent years, the use of polymeric energetic binders in the formulation of cast cured composite solids has presented growing interest. Hydroxyl-terminated polyethers with azido or nitro group polymers of low molecular weight are able to hold the fuel and oxidizer for propellants [1]. Glycidyl azide polymer (GAP) or poly(glycidyl azide) (PGA) is one of the most renowned and well-known azide polymers and is characterized as a low molecular weight, hydroxyl terminated difunctional liquid prepolymer with pendant azidomethyl groups on the main

polyether chain. In fact, it is a potential high energy material with a high positive heat of formation and low detonation sensitivity and hence it is considered both as a monopropellant and as a polymeric binder [2-5]. Several energetic polymers including azide or nitro polymers, such as poly(3-azidomethyl-3-methyloxetane) [poly(AMMO)] [6-9], poly[3,3-bis(azidomethyl)methyloxetane] [poly-(BAMO)] [8-11], poly(3-nitromethyl-3-methyloxetane) [poly(NMMO)] [12], poly[3,3-(nitratomethyl)methyloxetane] [poly(NIMMO)], and poly(glycidyl nitrate) [poly(GLYN)] [13, 14], have attracted the attention of researchers. Poly(ethylene glycol) (PEG) is widely used as a polymeric binder in solid rocket propellants [15, 16]. PEG and its two-component networks with urethane linkages between PEG and isocyanates have also been used as the binder in rocket propellants, *i.e.* nitrate ester plasticized propellants [17].

Microwave irradiation has been applied to number of processes, such as organic synthesis, polymer technology, pharmaceuticals, waste treatment, *etc*., and now a new area is high energy materials [18, 19]. Especially when heating is necessary, oil baths and heating jackets are the main tools used and such types of heating techniques are slow and time-consuming, and some times can lead to over heating and decomposition of the substrate and product. To this end, microwaves have been employed in chemistry to decrease the reaction times from hours to minutes, and to also increase yields and selectivity [20].

Considering the importance of GAPs and greener synthetic approaches, we have attempted the synthesis of PECHs and GAPs containing different diol units using microwave irradiation. The structures of the PECHs and GAPs containing different initiating diol units were confirmed by ^{1}H NMR, IR and UV spectral analysis. The thermal properties of the GAP diols were studied using differential scanning calorimetry (DSC).

2 Experimental

2.1 Materials and methods

All chemicals, namely, epichlorohydrin (**2**, ECH), ethylene glycol (1a, EG), propane-1,2-diol (1b, PD), hexylene glycol (HG) (**1c**, HG), diethylene glycol (1d, DEG), resorcinol (1e, RS), dichloromethane (DCM), N,N-dimethylformamide (DMF) and borontrifluoride etherate (BF_3-etherate) were used as synthetic grade and used without further purification. A SINEO Industrial microwave MAS II, with a reflux system, digital temperature display, temperature IR sensor and magnetic stirrer, was used to perform the reactions. The IR spectra were recorded in Nujol with a Perkin Elmer Spectrum One FTIR spectrophotometer. The UV

spectra were recorded with a CHEMITO SPECTRASCAN UV 2700. ^{1}H NMR spectra were recorded in $CDCl_3$ with an NMR Varian-300 spectrometer, using TMS as an internal standard. The thermal analysis of the polymers was performed with a DSC-200F3 SISIS Nano at a heating rate of 5 K/min under a nitrogen flow.

2.2 Synthesis of poly(epichlorohydrin)s (PECH)s containing different diol units (3) [21]

The ring-opening polymerization of epichlorohydrin was carried out in a 250 mL three-necked round bottom flask containing a magnetic stirrer follower, and equipped with a chloride guard tube, nitrogen line and a dropping funnel. A small amount of borontrifluoride etherate (1 mL) was added dropwise, using a dropping funnel, to a stirred solution of the diol (1a-e) in dichloromethane (5 mL) at room temperature and under a nitrogen atmosphere, and stirring was continued for 30 min. The reaction temperature was then lowered to 0 °C using an ice-salt bath and epichlorohydrin (**2**; 18.75 g) dissolved in dichloromethane (30 mL) was added dropwise over a period of 1 h, and stirring was continued for 4-5 h at the same temperature and then over night at room temperature. The reaction mixture was quenched by adding distilled water (50 mL). The organic layer was separated and washed with distilled water (5×25 mL) to remove unreacted diols and initiator and finally dried with fused calcium chloride. The solvent was removed under reduced pressure using a rotary evaporator to obtain the poly(epichlorohydrin) (PECH) (3a-e) in excellent yield (Table 1).

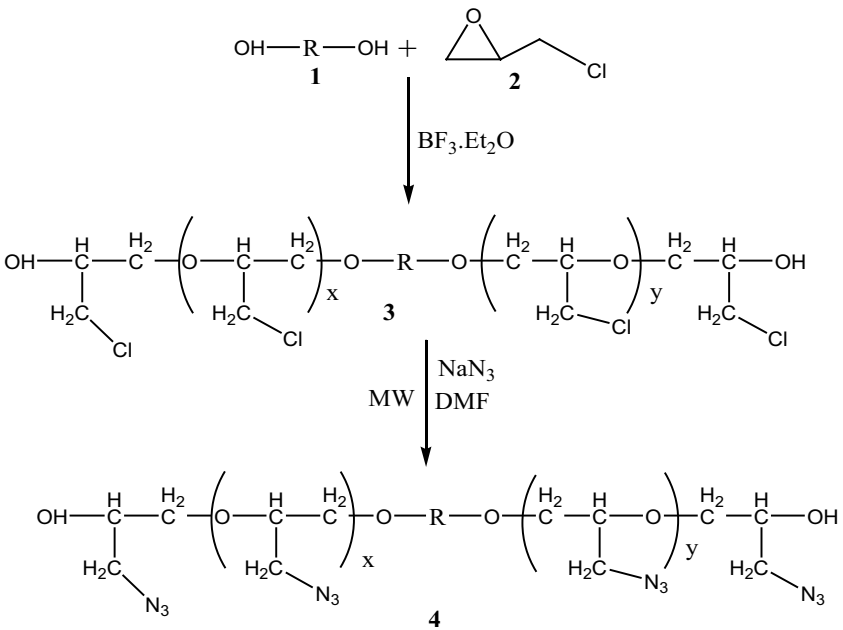
Table 1. Synthetic details of the preparation of the poly(epichlorohydrin)s containing different diol units

Entry	Polymer code	Epiclorohydrin, [g]	Diol, [g]	Yields, [%]
3a	PECH-EG	18.75	1.250	95.00
3b	PECH-PD	18.75	1.545	93.80
3c	PECH-HG	18.75	2.394	88.00
3d	PECH-DEG	18.75	2.150	94.00
3e	PECH-RS	18.75	2.230	85.00

2.3 Synthesis of glycidyl azide polymers (GAPs) (4a-e)

PECH-ED (**3a**, 2.0 g) in DMF (10 mL) was added to a three-necked round bottom flask equipped with a condenser, magnetic stirrer follower and calcium chloride guard tube. Sodium azide (1.455 g) was added to the above solution. The resulting reaction mixture was irradiated with microwave radiation at 600 W power, at 80 °C for 12 min. After completion of the reaction, the reaction mixture was cooled to room temperature and filtered to remove the salts and the

unreacted sodium azide. The filtered polymer solution was poured into distilled water (30 mL) where the polymer separated out. The polymer was repeatedly washed with water until the washings were free from azide and chloride ions. It was then dissolved in chloroform (20 mL) and dried with fused calcium chloride. The solvent was removed by vacuum distillation to obtain the pure GAP polymer (Scheme 1). The same procedure was adopted for the synthesis of all of the other GAPs (**4a-e**).



R = a) Ethylene glycol (EG),
b) Propane-1,2-diol (PD),
c) Hexylene glycol (HG),
d) Diethylene glycol (DEG),
e) Resorcinol (RS).

Scheme 1. Synthesis of GAP diol units.

3 Results and Discussion

GAP containing various diol units were synthesized successfully. The polyepichlorohydrin diols were prepared by the reactions of epichlorohydrin with different diols using borontrifluoride etherate as a Lewis acid catalyst at 0 °C. The

resulting GAP-diol polymer are amber/dark coloured liquids, soluble in DCM, chloroform, diethyl ether, N,N-dimethylformamide, and dimethylsulfoxide, *etc*. The polyepichlorohydrins contain –Cl as a good leaving group, which is easily replaced by $–N_3$ using sodium azide under microwave irradiation. The great advantages of this method are, it takes a very short time and is operated at a lower temperature than the reported methods. This method also gives a product of good purity and complete conversion of chloride to azide, similar to known methods. A detailed discussion of the GAP-diols is given in the spectral and thermal analysis sections.

3.1 Spectral analysis of polymers

The formation of the GAPs was confirmed by spectral analysis. The UV spectra of GAPs **(4a-e)** showed two peaks at 247 and 278 nm, attributed to the absorption of the nitrogen bonds of the azide groups in the polymer. The presence of these strong prominent peaks, corresponding to $CH_2{-}N_3$, indicated that all of the chlorine atoms in the PECHs had been replaced by azide groups in the azidation reactions.

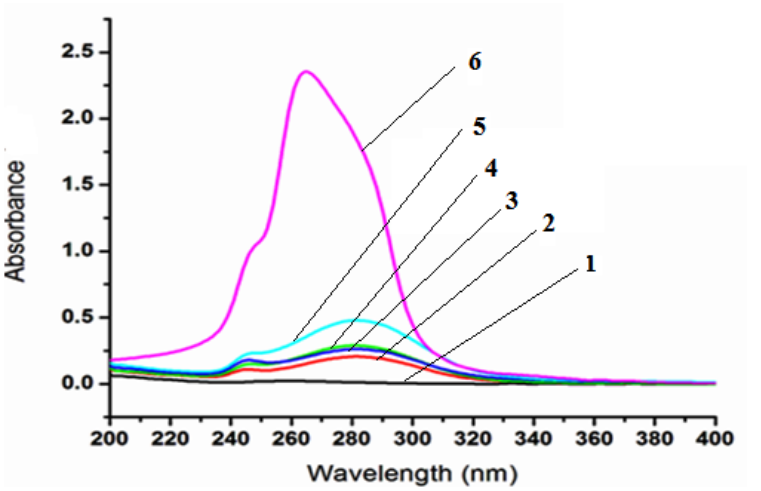


Figure 1. UV spectra of: 1) PECH-EG, 2) GAP-DEG, 3) GAP-EG, 4) GAP-HG, 5) GAP-PD, 6) GAP-RS

The FTIR spectra of the PECHs (3a-e) and GAPs (4a-e) are shown in Figures 2 and 3, respectively. The newly appeared absorption bands at 2080 and 1280 cm^{-1} correspond to the azide groups, formed on replacement of the Cl groups, whilst the corresponding C−Cl absorption band at 746 cm^{-1}

had disappeared (Figure 3). The presence of the prominent absorption bands corresponding to $CH_2{-}N_3$ groups and the complete disappearance of the CH_2Cl band confirmed that the chlorine atoms in the PECH had been replaced by azide groups in the azidation reactions.

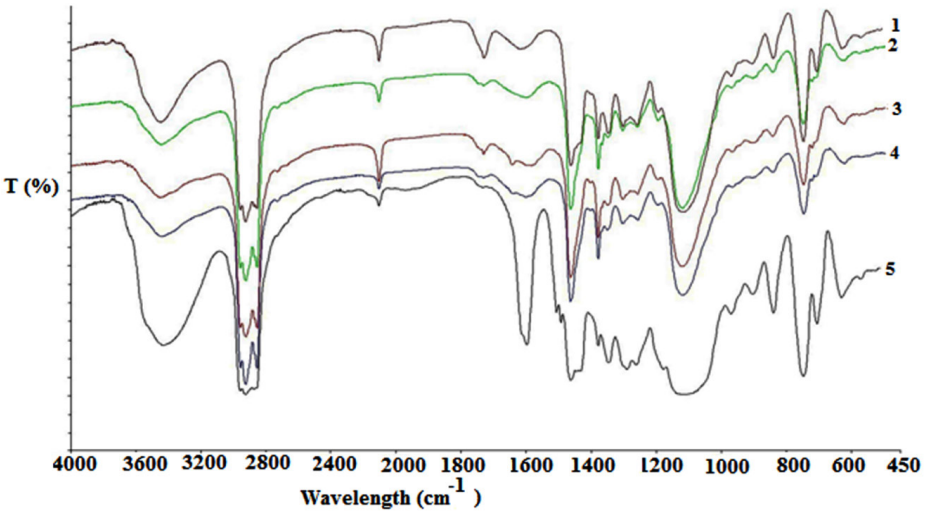


Figure 2. FTIR spectra of 1) PECH-PD, 2) PECH-HG, 3) PECH-EG, 4) PECH-DEG, 5) PECH-RS.

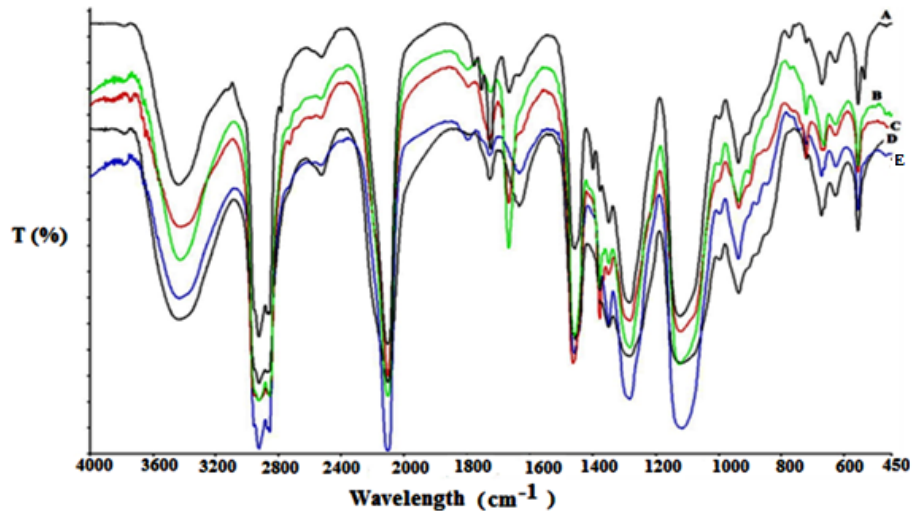


Figure 3. FTIR spectra of A) GAP-RS, B) GAP-DEG, C) GAP-HG, D) GAP-EG, E) GAP-PD.

The structures of glycidyl azide polymers containing the different initiating diol units were also confirmed by the ^{1}H NMR spectrum shown in Figure 4. The common peaks observed for all of the GAPs (**4a-e**) were at around δ 3.80 ppm (CH_2, CH protons of the polyether main chain) and δ 3.42 ppm (CH_2N_3 protons). In addition to the above peaks, the characteristic peaks corresponding to the protons of the different diol units were observed in these spectra, the peaks at δ 1.10-1.22 ppm, recognized as the CH_3 protons of propane diol (**4b**), δ 1.22-1.90 ppm recognized as the CH_3 and CH_2 protons of hexylene diol (**4c**), and δ 6.41-8.02 ppm, corresponding to the protons of the resorcinol diol (**4e**), in the polymeric chains of the GAPs.

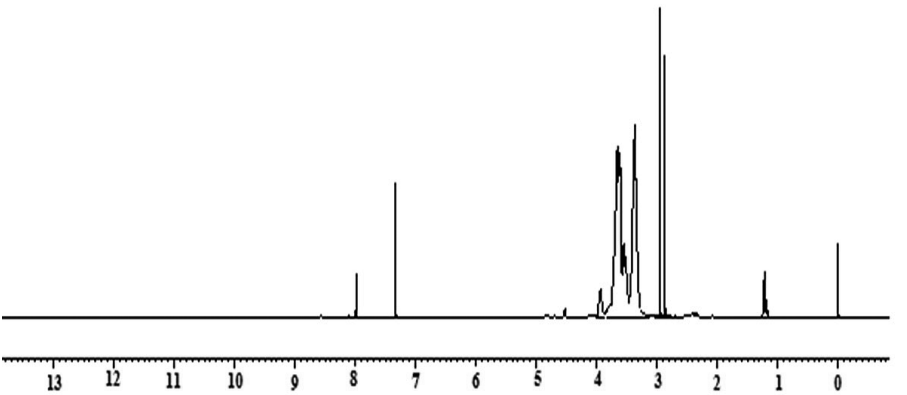


Figure 4. ^{1}H-NMR spectrum of GAP-EG.

3.2 Thermal studies

Thermal decomposition of the propellant binder plays an essential role in the combustion of composite solid propellants and so it was necessary to study the thermal decomposition of the synthesized GAPs. To determine the decomposition temperatures of the polymers, the DSC thermograms were recorded (Figure 5). A single main exothermic peak was observed between 232 and 244 °C in the DSC thermograms of all of the polymers (**4a-e**), and is mainly ascribed to the elimination of nitrogen by cleavage of the azide bonds from the azide pendant groups of the glycidyl azide polymers. A significant difference appeared in the decomposition temperatures of the azide pendant groups (Tazd) of the polymers (Table 2) and was attributed to the presence of different initiating diol units in the polymer chains. The sequence of Tazd of the various GAPs prepared using microwave methodology was GAP-HG> RS> EG> PD> DEG. The present results indicated that GAPs prepared using glycol units as initiating diols were with lower thermal

stability. The overall thermal stability of all GAPs synthesized using microwave was comparable to the GAPs preperaed by conventional method [20].

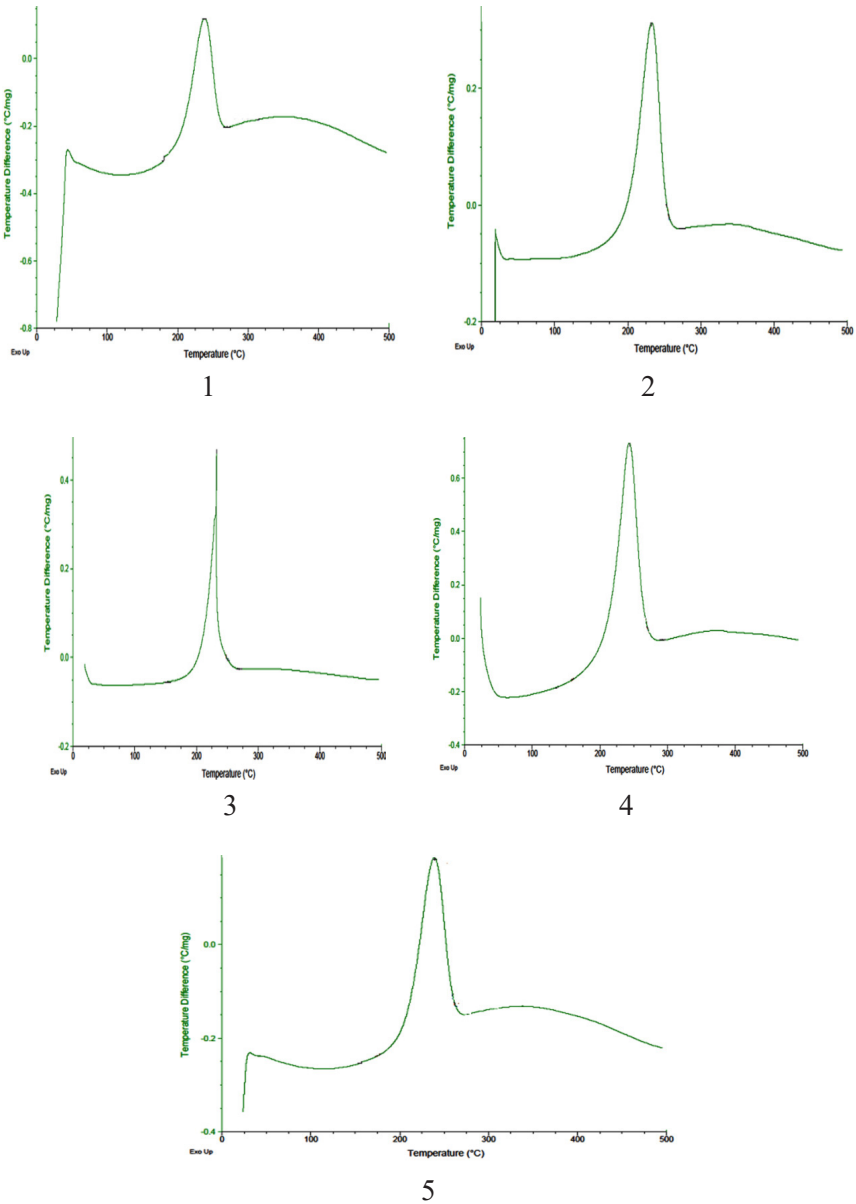


Figure 5. DSC thermograms of 1) GAP-EG, 2) GAP-DEG, 3) GAP-PD, 4) GAP-HG, 5) GAP-RS.

Table 2. Decomposition temperature of GAP-EG, GAP-PD, GAP-DEG, GAP-HG and GAP-RS

Entry	Polymer code	Decomposition temperature of azide groups in the polymer, [°C]
4a	GAP-EG	238
4b	GAP-PD	233
4c	GAP-HG	244
4d	GAP-DEG	232
4e	GAP-RS	239

4 Conclusions

The results of the present study reveal that the microwave-assisted synthesis of GAPs containing different diol units, in a short reaction time and at a low temperature, with high yields, could be achieved by adopting the methodology outlined. The synthesized GAPs were prepared by treating the corresponding PECHs with sodium azide, with microwave irradiation at 600 W power at 80 °C during 12 min. The structures of all of the synthesized PECHs and GAPs, containing different initiating diol units, were confirmed by spectral analysis. The thermal properties of the GAP-diols were studied using DSC. The azidation method used in the present study is of particular interest for scientists and technologists working in the field of high energy materials, in terms of economy of time and safer synthesis, with increased yield and purity of the products. The microwave technique appears to be a useful, greener approach for the synthesis of various promising high energy materials.

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5 References

[1] Kawamoto A.M., Diniz M.F., Lourenço V.L., Takahashi M.F.K., Keicher T., Krause H., Menke K., Kempa P.B., Synthesis and Characterization of GAP/BAMO Copolymers Applied at High Energetic Composite Propellants, *J. Aerosp. Technol.*

Manag., **2010**, *2*, 307-322.
[2] Eroglu M.S., Guven O., Thermal Decomposition of Poly(glycidyl azide) as Studied by High-temperature FTIR and Thermogravimetry, *J. Appl. Polym. Sci.*, **1996**, *61*, 201-206.
[3] Eroglu M.S., Guven O., Spectroscopic and Thermal Characterization of Poly(glycidyl azide) Converted from Polyepichlorohydrin, *J. Appl. Polym. Sci*., **1996**, *60*, 1361-1367.
[4] Frankel M.B., Grant L.R., Flanagan J.E., Historical Development of Glycidyl Azide Polymer, *J. Propuls. Power*, **1992**, *8*, 560-563.
[5] Badgujar D.M., Talawar M.B., Asthana S.N., Mahulikar P.P., Advances in Science and Technology of Modern Energetic Materials: an Overview, *J. Hazard. Mater*., **2008**, *151*, 289-305.
[6] Oyumi Y., Mitarai Y., Bazaki H., Thermal Decomposition of AMMO/AP Composite Propellants, *Propellants Explos. Pyrotech*., **1993**, *18*, 168-172.
[7] Sikder A.K., Reddy S., Review on Energetic Thermoplastic Elastomers (ETPEs) for Military Science, *Propellants Explos. Pyrotech*., **2013**, *38*, 14-28.
[8] Baopei X.U., Peter L.C., Chien J.C.W., Spiro(benzoxasilole) Catalyzed Polymerization of Oxetane Derivatives, *J. Polym. Sci*.,**1992**, *30*, 1899-1909.
[9] Talukder M.A.H., Lindsay G.A., Synthesis and the Preliminary Analysis of Block Copolymers of 3,3′-Bis(azidomethyl)oxetane and 3-Nitratomethyl-3′-methyloxetane, *J. Polym. Sci*., **1990**, *28*, 2393-2401.
[10] Kimura E., Oyumi Y., Kawasaki H., Maeda Y., Anan T., Characterization of BAMO, *Propellants Explos. Pyrotech*., **1994**, *19*, 270-275.
[11] Miyazaki T., Kubota N., Energetics of BAMO, *Propellants Explos. Pyrotech.*, **1992**, *17*, 5-9.
[12] Hanson-Parra D.M., Parra T.P., Thermal Properties Measurements of Solid Rocket Propellant Oxidizers and Binder Materials as a Function of Temperature, *J. Energ. Mater.*, **1999**, *17*, 1-48.
[13] Desai H.J., Cunliffe A.V., Hamid J., Honey P.J., Stewart M.J., Amass A.J., Synthesis and Characterization of α,ω-Hydroxy and Nitratotelechelic Oligomers of 3,3-(Nitratomethyl) Methyl Oxetane (NIMMO) and Glycidyl Nitrate (GLYN), *J. Polymer*., **1996**, *37*, 3461-3469.
[14] Desai H.J., Cunliffe A.V., Lewis T., Millar R.W., Paul N.C., Stewart M.J., Amass A.J., Synthesis of Narrow Molecular Weight α,ω-Hydroxytelechelic Poly(glycidyl nitrate) and Estimation of Theoretical Heat of Explosion, *J. Polymer*., **1996**, *37*, 3471-3476.
[15] Jizhen L., Xuezhong F., Xiping F., Fengqi Z., Rongzu H., Compatibility Study of 1,3,3-Trinitroazetidine with Some Energetic Components and Inert Materials, *J. Therm. Anal. Calorim*., **2006**, *85*, 779-784.
[16] Lin Z., Han X., Wang T., Li S., Effects of Adding Nano Metal Powders on Thermooxidative Degradation of Poly(ethylene glycol), *J. Therm. Anal. Calorim*., **2008**, *91*, 709-717.
[17] Jian X.-X., Xiao L.-Q., Zhou W.-L., Xu F.-M., Synthesis and Characterization of

PMMA/PEG-TPE Semi-interpenetrating Polymer Networks, *Polym. Bull.*, **2009**, *63*, 225-233.

[18] Saikia A., Sivabalan R., Gore G.M., Sikder A.K.; Microwave-assisted Quick Synthesis of Some Potential High Explosives, *Propellants Explos. Pyrotech*., **2012**, *37*, 540-543.

[19] a) Badgujar D.M., Mahulikar P.P.,Talwar M.B., Asthana S.N., Novel Synthesis of 1,1,3,3,5-Tris-spiro(N,N'-dinitroethylenediamino)cyclotriphosphazene Using Solid Supported Bismuth Nitrate, *Org. Chem. Indian Journal*, **2007**, *3*,185-187; b) Badgujar D.M., Talawar M.B., Asthana S.N., Venugopalan S., Subhananda R.A., Mahulikar P.P., Microwave Assisted Facial Synthesis of {1/1,3-bis/1,3,5-tris-[(2-nitroxyethylnitramino)-2,4,6-trinitrobenzene]}Using Bismuth Nitrate Pentahydrate as an Eco-friendly Nitrating Agent, *J. Hazard. Mater*., **2008**, *152*, 820-825; c) Badgujar D.M., Talawar M.B., Asthana S.N., Mahulikar P.P., Synthesis and Characterization of Methyl Nitramino- 2, 4, 6-Trinitrobenzenes Using Bismuth Nitrate Pentahydrate as an Eco-friendly Nitrating Agent, *J. Sci. Ind. Res*., **2010**, *69*, 208-210; d) Badgujar D.M., Talawar M.B., Asthana S.N., Mahulikar P.P., Eco-Friendly Nitration of Aromatic Compounds Using Different Solid Supports, *Chem. Sustainable Develop*., **2009**, *17*, 323-325.

[20] Stuerga D., Gonon K., Lallemant M., Microwave Heating as a New Way to Induce Selectivity Between Competitive Reactions. Application to Isomeric Ratio Control in Sulfonation of Napthalene, *Tetrahedron*, **1993**, *49*, 6229-6234.

[21] Mohan Y.M., Raju M.P., Raju K.M., Synthesis, Spectral and DSC Analysis of Glycidyl Azide Polymers Containing Different Initiating Diol Units, *J. Appl. Polym. Sci*., **2004**, *93*, 2157-2163.